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ORIGINAL PAPER

Effects of Excess or Deficiency of Oxygen Content on the Electronic Structure of High-T_c Cuprates

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Abstract Band structure calculations are presented for large supercells of Ba_2CuO_4 (BCO) with O-vacancies in planar or apical positions, and of superoxygenated La_2CuO_4 (LCO) with oxygen interstitials in the La_2O_2 layers. It is found that apical oxygen vacancies in BCO act as electron dopants and makes the electronic structure similar to that of hole doped LCO. Excess oxygen interstitials forming wires in the La_2O_2 layers of LCO are shown to yield a much larger density-of-states at the Fermi energy than for the stoichiometric compound related with a segmentation of the Fermi surface. Antiferromagnetic (AFM) spin fluctuations are strengthened by O-vacancies in BCO as well as by oxygen interstitials in LCO, but are strongly suppressed in O-deficient LCO. Our results indicate the complexity of doping by O-vacancies, and by ordered defects that are a significant factor controlling the electronic properties of cuprates.

Keywords Cuprates · Electronic structure · Oxygen defects

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1 Introduction

High-T_c cuprate superconductors in their normal state show many unusual properties such as pseudogaps, stripe-like charge/spin modulations with particular energy/doping dependencies, Fermi-surface (FS) "arcs" in the diagonal direction, 'kinks' and 'waterfalls' in the band dispersions, anomalous isotope effect, and phonon softening [1, 2]. It is generally believed that stripe-like modulations of the Cu-spin arrangements are important for doped cuprates. Band results for long '1-dimensional' (1-D) supercells, calculated by the Linear Muffin-Tin Orbital (LMTO) method in the local spin-density approximation (LDA), show large spin-phonon coupling (SPC) within the CuO planes [3, 4]. The LMTO results have been used to parameterize the strength of potential modulations coming from phonon distortions and spin waves of different length [5]. Phonon softening, dynamical stripes, correlation between $\bar{q}$ and x, smearing of the non-diagonal part of the FS, and abrupt disappearance of spin fluctuations at a certain T^*, are all possible consequences of SPC within a rather conventional band picture [5, 6]. Weak ferromagnetism is a possibility at very high hole doping levels [7, 8]. The focus has been for many years on the intrinsic electronic response of the CuO_2 plane following electronic doping pushing the chemical potential away from half filling. The details of the structure of spacer layers intercalated between the CuO_2 planes and the role of dopants, atomic substitutions, defects or oxygen interstitials inserted there to convert the undoped antiferromagnetic CuO_2 plane into a superconductor has not been much considered so far.

Recently there has been growing interest to control the superconducting T_c by changing the structure of the spacer layers. It is known that maximum superconducting T_c at optimum doping increases from 20 to 130 K by manipulation

of the spacer layers structure [9] and the spatial distribution of defects inserted there. For example the maximum superconducting T_c in La_2CuO_4 (LCO) achieved through La/Sr or La/Ba exchange is 35 K while with the maximum T_c in superoxygenated $La_2CuO_{4+\delta}$ can reach 45 K. Recently the ordering of oxygen interstitials has been shown to control the superconducting T_c [10, 11]. High T_c's have been reported for oxygen deficient $Sr_2CuO_{4-\delta}$ [12–14] and in other cuprates with ordered defects [15]. Moreover the dopants and their self organization have been shown to control the critical temperature in pnictides [16] and chalcogenides [17].

Here we present aspects of our results of band structure calculations on supercells of Ba_2CuO_4 (BCO) or La_2CuO_4 (LCO) with various distributions of O-defects for the purpose of gaining insight into how the electronic structure and magnetic interactions are modified by the presence of such defects. For oxygen deficient structures it matters if the vacancies are located within the CuO_2 planes or in apical positions. In the latter case the vacancies act as electron dopants of the Cu-d band, so that BCO with a substantial apical-vacancy concentration would approach the band filling of hole doped LCO. Excess oxygen interstitials inserted in the rocksalt La_2O_2 layers of LCO occupy the oxygen interstitial positions as oxygen ions in fluorite Nd_2O_2 spacer layer of Nd_2CuO_4.

We show here the breakdown of the common rigid band model for doped CuO_2 planes. Defects induce a band folding and opening of partial gaps at specific points in the k-space and produce multiple mini-bands crossing the Fermi level as has been proposed [18]. Moreover the ordered oxygen interstitials yield a much larger density-of-states at the Fermi energy than for the stoichiometric compound, favoring enhanced spin fluctuations.

A more complete discussion of these results will be undertaken elsewhere [19, 20].

2 Method of Calculation

Ab-initio LDA-LMTO band calculations are carried out for supercells of $R_2CuO_{4\pm\delta}$, with R = La or Ba (LCO or BCO). In the case of oxygen vacancies in LCO and BCO, the calculations are based on supercells with a total of 112 sites [19]. The supercell is obtained via a $2 \times 2 \times 2$ extension of the basic antiferromagnetic (AFM) cell, $R_{32}Cu_{16}O_{64-n_V}$, where n_V is the number of O-vacancies in the cell. Different concentrations $\delta = n_V/16$ of vacancies either in the planes (P) or in apical (A) positions are realized through a randomized (not clustered) distribution of vacancies in $R_2CuO_{4-\delta}$.

For simulating ordered stripe-like interstitial oxygens, we first insert empty spheres in all interstitial positions at $(\frac{1}{2}, 0, \frac{1}{2}c)$ and $(0, \frac{1}{2}, \frac{1}{2}c)$, and then occupy one or two of these positions with additional oxygen interstitials. In total, this yields a supercell with 72 sites for a $4 \times 1 \times 1$ extension of the basic AFM cell along the diagonal [1, 1, 0]-direction, $La_{16}Cu_8O_{32+N}$, where N is the number of additional oxygens. There are one or two adjacent rows of additional O in the supercells [20]. The atomic spheres are reduced compared to the calculations for the 112-site supercell, but the results for defect free LCO are very similar in the two sets of calculations.

Spin-polarized calculations are made with applied magnetic fields on selected Cu-sites in order to generate AFM order. Other details of our band calculation methods have been published elsewhere [19–21]. It should be noted that a rigid band picture [22] or its variants [23] have often been invoked in describing the doping evolution of the overdoped and optimally doped cuprates [24, 25]. Our large supercell treatment here goes beyond the simple rigid band model or possible mean-field type approaches [26, 27] to elucidate the local electronic and magnetic properties of the system.

3 Results for O-Deficient BCO and LCO

Unpolarized calculations show that apical or planar oxygen vacancies act very differently with respect to d-band filling and charge on Cu [19]. Apical vacancies in BCO lead to a charge transfer toward Cu and an upward shift of E_F relative to the d-band, so that the band structure of BCO with many vacancies can approach that of hole doped LCO.[1] Apical vacancies in LCO have a similar but weaker doping effect, whereby LCO becomes electron doped. Vacancies in the planes of LCO lead to hole doping, while in BCO the effect on doping is small. These results are interesting in view of recent reports of high T_c in oxygen deficient SCO [14], although possibility of some type of ordering has been implicated [13, 15]. A question that arises naturally in this connection is whether the propensity for AFM fluctuations correlates with the effective doping level, since spin fluctuations are probably involved in the mechanism of superconducting pairing. Accordingly, in our calculations we mimic an AFM order by applying positive or negative magnetic fields on every second Cu. We have taken the AFM structure and the field amplitudes to be identical in all cases investigated in order to make direct comparisons between BCO and LCO with different types of defect.

Our main results are summarized in Table 1. For vacancies in CuO planes of BCO there is, in addition to the weak hole doping within the Cu-d band, a tendency toward stronger AFM fluctuations. The enhancement is similar for

[1] Note that Ba and Sr have one less electron than La, which makes BCO and SRO, Sr_2CuO_4, an extremely hole doped version of LCO.

Table 1 Valence charge Q_{Cu} (in electrons/per Cu), the change ΔQ_{Cu} with respect to the undoped case, and the magnetic moment m (in μ_B per Cu) as a function of the number (n_V) of planar (P) or apical (A) oxygen vacancies in BCO and LCO. A magnetic field of ±2.5 mRy was applied to generate AFM order on Cu

n_V	BCO			LCO		
	Q_{Cu}	ΔQ_{Cu}	$\bar{m}$	Q_{Cu}	ΔQ_{Cu}	$\bar{m}$
9 (P)	10.055	−0.010	0.024	10.332	−0.063	0.010
8 (P)	10.056	−0.009	0.022	–	–	–
5 (P)	10.057	−0.007	0.024	10.368	−0.026	0.025
1 (P)	10.062	−0.002	0.021	10.395	−0.000	0.073
0	10.064	0.000	0.020	10.394	0.000	0.069
1 (A)	10.071	0.007	0.021	10.420	0.026	0.069
5 (A)	10.107	0.043	0.028	10.450	0.056	0.024
8 (A)	10.145	0.081	0.038	–	–	–
9 (A)	10.163	0.099	0.035	10.456	0.062	0.022

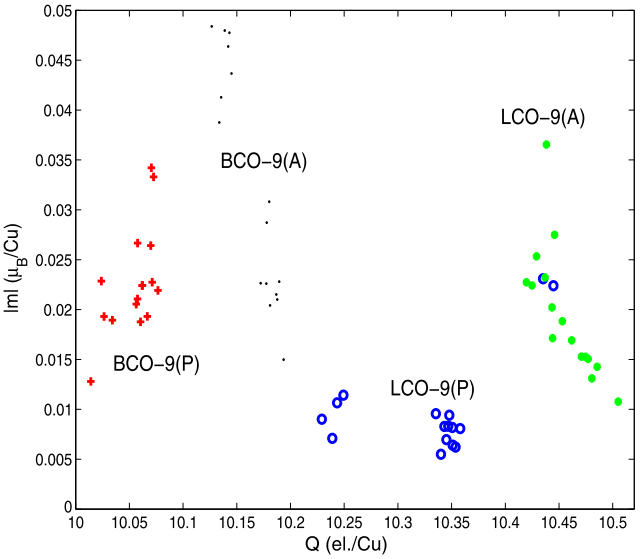

Fig. 1 Absolute value of the magnetic moment m as function of the valence charge for each Cu-atom in BCO and LCO with nine apical or planar O-vacancies

vacancies on the apical positions, in spite of the clear electron doping in this case. The evolution of AFM fluctuations for O-vacancies in LCO is very different. Undoped LCO has strong enhancement of AFM waves that leads to a stable AFM configuration and an insulator. Well converged LSDA calculations do not find this state, but it has been shown that LMTO calculations with off-center linearization energies of the Cu-d states lead to slight localization and stable AFM order [29]. Both apical and planar vacancies quickly suppress the tendency for antiferromagnetism as seen in Table 1. This agrees qualitatively with early calculations for a single O vacancy in small unit cells of LCO [28].

Interestingly, we find that the electron doping effect in BCO with apical vacancies is strong, and one may ask if the properties of such crystals are similar to those of hole doped LCO. Our results indicate that it is not exactly so, since antiferromagnetism in BCO with the highest electron doping is stronger than in LCO where maximal hole doping is made via planar O-vacancies. In LCO, it seems that breaking the near neighbor order through apical or planar O-vacancies will effectively quench AFM fluctuations, much like the effect of Sr doping. An example can be seen in Fig. 1, where the local moment on Cu is plotted as a function of the local Cu valence charge for configurations with nine O-vacancies. These results suggest that local order is probably an important factor for antiferromagnetism. The increasing strength of spin fluctuations with increasing number of apical vacancies provides a possible explanation for why oxygen deficient SRO can have a higher T_c than the traditional hole doped LCO. Doping is usually thought to be determined by the La vs. Sr/Ba substitution, but our results show that oxygen deficiency may have large effects on doping as well. For instance, electron doping usually carried out through La/Nd–Ce substitution is accompanied with a structural change of the apical O position, but our results show that apical O-vacancies in LCO could provide an alternate route for electron doping keeping the structure intact.

4 Results for Stripes of Oxygen Interstitials in the Spacer Layers

Rows of single or double interstitial O's oriented along [1,1,0] make the DOS at E_F larger than in undoped LCO by factors of 2.5 or 3, respectively, see Fig. 2. The new O-p bands associated with the interstitials are found to lie a few eV below E_F, but hybridization effects make the bands at E_F narrower. The interstitial oxygens and the neighboring atoms acquire most of the additional DOS. This increase in DOS comes about because the band at E_F is broken up by the new periodicity with smaller dispersion between the resulting small gaps. A folding of the original almost circular LCO Fermi surface (FS) into the new Brillouin Zone (BZ), given by Γ–R–X_3–M_3, produces a FS similar to the one in Fig. 3. The computed FS for the undoped supercell ($N = 0$) of LCO agrees even more with the model where circular FS in the original BZ has been downfolded into the BZ of the supercell. One difference is that the FS's for the supercells containing extra O are segmented with gaps between the branches. The three branches in Fig. 3 corresponds to different sections of the circular FS in the original BZ. Furthermore, the calculated band mass increases when one or two O atoms are added, and bands become gapped near the boundaries of the new BZ. A general upward displacement of the FS branch in the left part of Fig. 3 can be understood from an increased radius of the original FS. This represents

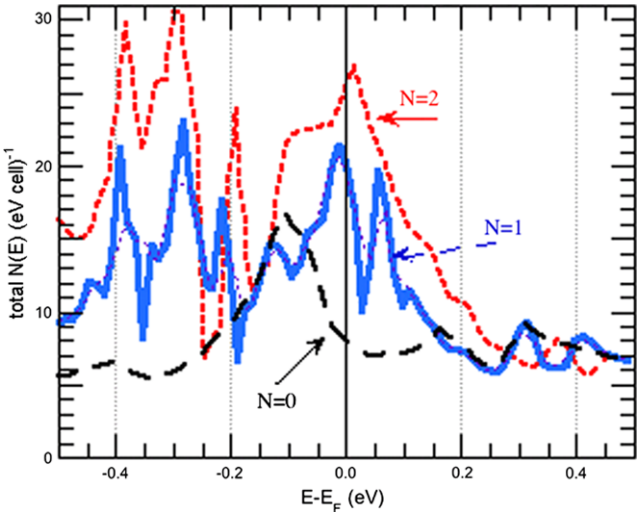

Fig. 2 The total DOS of the undoped $La_{16}Cu_8O_{32}$ near the Fermi level is compared with the DOS of doped superoxygenated La_2CuO_4 with additional $N = 1$ and $N = 2$ oxygen interstitial in the supercell

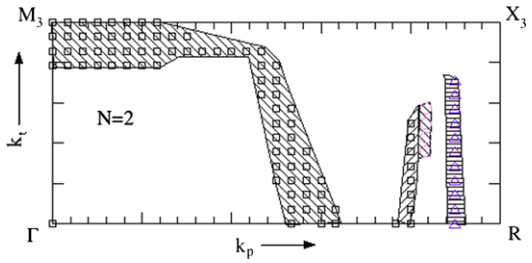

Fig. 3 The calculated FS for $La_{16}Cu_8O_{32+N}$ for $N = 2$. This FS can be understood from a folding of the original circular FS into the Brillouin Zone of the supercell (given by Γ–R–X_3–M_3), but the partial gaps appears only for $N > 0$

hole doping, which is consistent with effective charges on Cu: Addition of each interstitial O in the cell removes about 0.04 electrons from each Cu.

The new periodicity sets up a potential modulation along the unit cell and as expected induces weak pseudogaps in the DOS near E_F. It turns out that E_F falls on a DOS peak above the gap energy, both for one and two extra oxygen atoms. Thus, the observation of ordering of oxygen interstitials [11, 30] might be a promising way for creating potential modulations, pseudogaps and enhanced $N(E_F)$ for boosting superconductivity [21]. Furthermore, FS segmentation and small gaps separating mini bands could provide favorable conditions for Lifshitz transitions in connection with other mechanisms for enhanced T_c [31]. Notably, the enhanced $N(E_F)$ favors AFM fluctuations in general [32]. The calculation of modulated AFM spin waves shows a moderate increase of the exchange enhancement when one or two O-interstitials are added, but the effect concerns mostly Cu sites far from the interstitials. The strong hybridization with the additional O-p electrons, which are not magnetically active, is probably the cause of the limited effect on nearby Cu sites.

5 Conclusion

Our study shows that electronic properties of cuprates can be modified substantially by the presence of oxygen defects. In particular, vacancies among apical and planar oxygen sites lead to very different charge filling within the Cu-d band, and strong changes in the AFM couplings in the system. Moreover, AFM fluctuations in BCO and LCO behave quite differently as a function of doping. The effective doping depends not only on La/Ba substitutions, but also on the specific nature of oxygen vacancies. For excess O, we follow the suggestions from experiments and assume that interstitial oxygens order into stripes. The new periodicity makes the DOS high at E_F, which leads to some enhancement of AFM fluctuations. The FS branches remain fairly intact and identifiable for different doping, but mini-gaps are formed to make the FS segmented. Heavier band masses are evident as well as a slight hole doping for increasing O content. These changes are normally favorable to a higher T_c.

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